

Langevin equation with colored noise for constant-temperature molecular dynamics simulations

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We discuss the use of a Langevin equation with a colored (correlated) noise to perform constant-temperature molecular dynamics simulations. Since the equations of motion are linear in nature, it is easy to predict the response of a Hamiltonian system to such a thermostat and to tune at will the relaxation time of modes of different frequency. This allows one to optimize the time needed to thermalize the system and generate independent configurations. We show how this frequency-dependent response can be exploited to control the temperature of Car-Parrinello-like dynamics, keeping at low temperature the electronic degrees of freedom, without affecting the adiabatic separation from the vibrations of the ions.

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Solving Hamilton's equations leads to sampling of the microcanonical constant-energy distribution, but in real-life experiments it is the temperature that is kept constant. Reproducing this condition in computer simulations is of great importance for the investigation of a large class of physical, chemical and biological problems. Several approaches have been proposed to modify Hamilton's equations in order to perform constant-temperature dynamics (see e.g. Refs. [1–4]). Many of these [1, 4] rely on stochastic methods, which are a natural choice for modeling the interactions with an external heat bath, and which display excellent ergodic behavior due to their random nature. A good thermostat should be able to rapidly enforce the correct probability distribution, and generate uncorrelated configurations, which are necessary to compute ensemble averages. The efficiency of the thermostat is particularly important in *ab initio* simulations, because of their high computational cost. The stochastic thermostats used so far are based on Markovian equations of motion, and imply no memory of the past trajectory of the system.

Markovian random processes are, however, only a subset of all possible stochastic processes. Furthermore, the Mori-Zwanzig theory ensures that whenever some degree of freedom is integrated out, the dynamics of the remaining degrees of freedom are described by a non-Markovian Langevin equation, with a finite-range memory function [5–7]. Hence, in the quest for a better thermostat, and considering the thermostat as arising from a set of bath variables whose effect is integrated out, it is natural to explore the effect of using a non-Markovian Langevin equation to perform constant-temperature molecular dynamics. In this Letter we will show that, by using colored noise, it is possible to influence in a different manner the different vibrational modes of the system. Therefore the thermostat can be adjusted to the system under study, and its performance optimized in a precise and predictable fashion. This is, to our knowledge, the first

time that a colored Langevin equation has been employed in atomistic simulations.

An area which would greatly benefit from an improved, tunable thermostat is that of Car-Parrinello (CP)-like, extended Lagrangian schemes [8]. The idea behind this approach is very general, as it applies to any system where the forces are the result of an expensive optimization procedure. This process is circumvented by extending the dynamical degrees of freedom (DOF), so as to include the parameters to be optimized, and introducing an artificial dynamics which allows these extra variables to be maintained close to the ground state, by adiabatic decoupling from the other degrees of freedom. In the prototypical example of CP molecular dynamics (CPMD) a fictitious mass is assigned to the electronic DOF so that they can be evolved at the same time as the ionic DOF. If the fictitious mass is small enough, the dynamics of the electrons are adiabatically separated from the dynamics of the ions. Hence, the electrons are kept close to the ground state, while the nuclei are evolved at the correct temperature. This same technique can be used in classical simulations that use polarizable force fields, where the electronic DOF describe the charge polarization of the system [9, 10]. Similar approaches have also been suggested in the field of rare-events sampling, to separate the oscillations of the microscopic degrees of freedom from those of a few selected slow reaction coordinates [11].

Controlling the temperature in these CP-like techniques requires that one acts separately on the ionic degrees of freedom, which must sample the correct canonical ensemble, and on the variational parameters, which must always remain at low temperature to minimize the error in the forces [12]. Traditional stochastic thermostats allow for a highly ergodic sampling of all the degrees of freedom, irrespectively of their frequency. This is beneficial for the ionic DOFs but causes the breakdown of adiabatic separation. For this reason, deterministic thermostats of the Nosé-Hoover (NH) type [2] have been

adopted. However the original NH thermostat has well-known ergodicity problems, and the extension to Nosé-Hoover chains is normally used [3]. This comes though at the price of introducing a large number of parameters, whose effect on the ions dynamics is not easy to predict and control. In the following we show that by using correlated noise it is possible to tune the coupling of a stochastic thermostat with the various degrees of freedom. This allows one not only to use Langevin dynamics in CP-like methods, but also significantly improves the sampling of the target ensemble, because the thermostat is tailored to the system under study, in a predictable and controlled fashion.

We consider here a system described by coordinates q_i , momenta p_i and masses m_i , interacting via a potential $U(q)$, where q is the set of q_i 's. The colored Langevin equations [5, 6] read

$$\begin{aligned}\dot{q}_i(t) &= p_i(t)/m_i \\ \dot{p}_i(t) &= f_i[q(t)] - \int_0^t dt' \mathcal{K}(t-t') p_i(t') + \zeta_i(t)\end{aligned}\quad (1)$$

where $f_i = -\partial U/\partial q_i$ are the forces, $\mathcal{K}(t)$ is the memory kernel and $\zeta(t)$ is a vector of independent Gaussian noises. In order to set the temperature to a chosen value T , the noise term $\zeta(t)$ needs to be related to the memory kernel by the fluctuation-dissipation theorem $\langle \zeta_i(t) \zeta_j(t') \rangle = \delta_{ij} m_i T \mathcal{K}(t-t')$.

The non-Markovian Eqs. (1) might seem at first too complex to be used in practical applications. However, for a rather general form of the memory kernel, $\mathcal{K}(t) = \Re \sum_k c_k e^{-t(\gamma_k + i\omega_k)}$ with $\gamma_k > 0$, it is possible to rewrite Eq. (1) in an equivalent Markovian form by introducing a set of auxiliary momenta [13, 14]:

$$\begin{aligned}\dot{q}_i(t) &= s_{0i}(t)/m \\ \dot{\mathbf{s}}_i(t) &= (f_i[q(t)], 0, \dots, 0)^T - \mathbf{A} \mathbf{s}_i(t) + \mathbf{B} \boldsymbol{\eta}_i(t).\end{aligned}\quad (2)$$

Here $\mathbf{s}_i = (p_i, s_{i1}, \dots, s_{iN})^T$ is a $N+1$ dimensional vector, whose first component is the canonical momentum p_i associated to the i -th DOF, and $\boldsymbol{\eta}_i$ is a vector of Gaussian white noises, with $\langle \eta_{ik}(t) \eta_{jk'}(t') \rangle = \delta_{ij} \delta(t-t') \delta_{kk'}$. The real-valued matrices \mathbf{A} and \mathbf{B} determine the dynamics of p_i , and can be related to $\mathcal{K}(t)$ by extending the arguments of Ref. [13], as will be discussed elsewhere.

In order to illustrate some of the effects of using a colored noise, we study the simple case in which

$$\mathbf{A} = \frac{1}{\tau_F} \begin{pmatrix} 0 & -\sqrt{\gamma \tau_F} \\ \sqrt{\gamma \tau_F} & 1 \end{pmatrix}, \quad \mathbf{B} = \sqrt{\frac{2Tm_i}{\tau_F}} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}. \quad (3)$$

This choice leads to the stationary distribution

$$\bar{P}(q, p, s_1) \propto \exp \left[-\frac{1}{T} \left(\frac{p^2}{2m} + \frac{s_1^2}{2m} + U(q) \right) \right],$$

corresponding to the desired canonical ensemble for q and p . The memory kernel and its power spectrum are

$$\mathcal{K}(t) = \frac{\gamma}{\tau_F} e^{-|t|/\tau_F} \quad \text{and} \quad \mathcal{S}(\omega) = \frac{\gamma}{\pi} \frac{1}{1 + \tau_F^2 \omega^2} \quad (4)$$

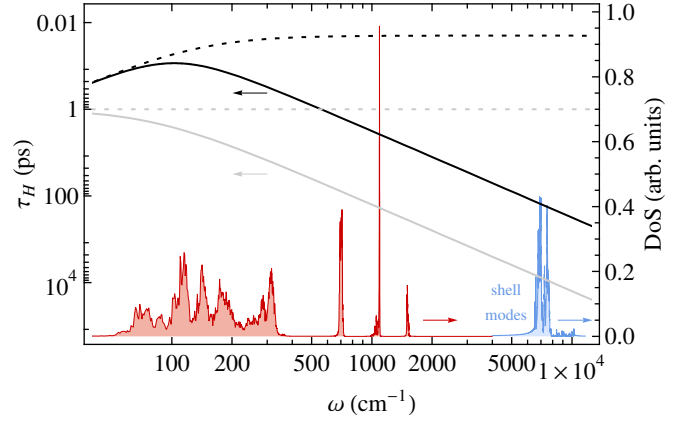


FIG. 1: (color online) The autocorrelation time of the total energy for harmonic oscillators of frequency ω [Cf. Equation (5)] is plotted for different values of the thermostat parameters. Dark curves correspond to high friction ($\gamma^{-1} = 20$ fs) whereas light ones correspond to a more gentle thermostat ($\gamma^{-1} = 1$ ps). Dotted lines correspond to white noise ($\tau_F = 0$) and full ones to colored noise with $\tau_F = 2$ fs. The curves are superimposed on the vibrational density of states (DoS) for a polarizable force-field simulation of crystalline calcite, which was obtained from the Fourier transform of the velocity-velocity autocorrelation function. For reference, we report the shell vibrational modes as obtained from a run where we artificially heated the shells to 300 K.

respectively. Thus the friction γ determines the intensity of the kernel and τ_F the autocorrelation time of the noise. For the purpose of this work, one can consider $S(\omega)$ to be a low-pass filter for the noise, which has the cutoff frequency τ_F^{-1} . Clearly, when $\tau_F \rightarrow 0$ the white-noise limit is recovered.

We consider the dynamics of a set of harmonic oscillators. In this case Eqs. (2) are fully linear, and the autocorrelation time for the total energy of an eigenmode of frequency ω can be explicitly evaluated [6, 15]:

$$\tau_H(\omega) = \frac{\gamma}{4\omega^2} + \frac{1}{\gamma} + \frac{\omega^2 \tau_F^2}{\gamma}. \quad (5)$$

We take $\tau_H(\omega)$ as a measure of the time needed for the thermalization of each individual normal mode. For a white noise ($\tau_F = 0$), τ_H decreases with ω until it reaches a plateau at $\tau_H = 1/\gamma$, while for $\tau_F \neq 0$, the autocorrelation time has a minimum at $\omega = \sqrt{\gamma/(2\tau_F)}$ and grows quadratically thereafter. By properly adjusting τ_F , one can select which modes are going to be maximally coupled with the thermostat, and thus reduce the coupling of the thermostat to the fastest modes (see also Fig. 1).

We next consider the application of the colored-noise thermostat, with the parameters of Eq. (3), to classical MD simulation using a polarizable force field. Here the electronic DOF are represented by charged shells, bound with harmonic potentials to the corresponding atomic cores. We couple a colored-noise thermostat to the ions, at the target temperature, and choose the filtering time τ_F in such a way that the impact on the electronic DOF is minimal. At the same time, we apply a zero temperature

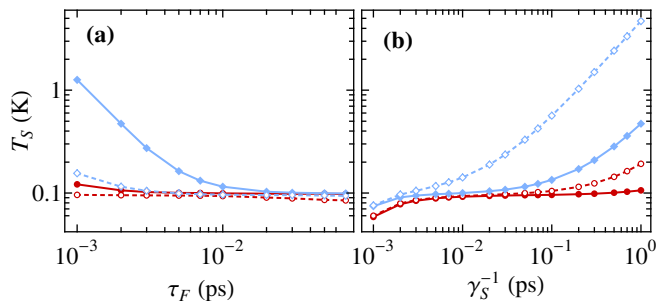


FIG. 2: (color online) Shell temperature (T_S) for calcite as a function of the thermostat parameters. Simulations have been performed for the discrete series of values indicated by arrows on the horizontal axes. The points are joined by continuous lines, for clarity sake. In both panels we distinguish the strength of the ion thermostat by the line color. Darker or lighter (red or blue in the online version) curves correspond respectively to a strong ($\gamma^{-1} = 20$ fs) or mild ($\gamma^{-1} = 1$ ps) friction. In panel (a) we plot T_S against τ_F , and we choose two extreme values of the shell friction, $\gamma_S^{-1} = 1$ ps and $\gamma_S^{-1} = 50$ fs, which are represented respectively with full and dashed lines. In panel (b) we plot the dependence of T_S versus γ_S . Here full and dashed lines correspond respectively to a physically meaningful filter ($\tau_F = 2$ fs) and to white noise ($\tau_F = 0$).

thermostat of friction γ_S to the electrons. This latter thermostat is memory-less, so that it couples optimally with the fast electronic modes. Such a simulation scheme amounts to a non-equilibrium dynamics, in which heat is injected into the ionic DOF and systematically subtracted from the electronic ones. In spite of the stochastic nature of these equations it is still possible to introduce a conserved quantity that measures the accuracy of the integration. This can be obtained by accumulating the change in kinetic energy due to the thermostat [4, 16–18]. However, at variance with Refs. [4, 16], the conservation of this quantity does not rigorously measure the sampling accuracy.

As an example we consider the simulation of crystalline calcite, modeled by a polarizable force field [17]. The Ca^{2+} ions are treated as non-polarizable, while the polarization of the CO_3^{2-} anions is described by a charged shell attached to each oxygen. The thermostats are applied to the non-polarizable ions and, in the case of the oxygens, to the center of mass of the system formed by the ion plus its shell. Meanwhile, the electronic temperature is controlled by the damping of the velocity of the shells relative to the partner O ions. The vibrational density of states in the absence of any thermostat can be used as an approximate guide to the choice of the colored thermostat parameters (see Fig. 1). In real-life, anharmonicity will introduce some coupling between the normal modes, so that deviations from the predictions of Eq. (5) are expected. However, at least in the case of quasi-harmonic modes, they will most likely reduce $\tau_H(\omega)$. Thus, one can safely use the analytical estimate to tune the thermostat parameters beforehand, without having to perform time-consuming tests on the real system.

We simulated [19] a box containing 96 CaCO_3 units,

with a timestep of 1 fs, performing *NVT* runs with target temperature $T = 300$ K. We performed systematic tests by varying τ_F , γ and γ_S (Fig. 2). The averages have been computed from 1 ns-long runs, where we discarded the first 100 ps for equilibration. Within a large range of parameters, the procedure performs as expected: the temperature of the shells remains below a few K, and the ions equilibrate to the desired temperature. As τ_F is set to a value different from zero, the heat transferred to the electronic DOF is reduced. However, some care must be taken in choosing the friction γ_S , because the shell thermostat can induce a small drag on the ions which results in an ionic temperature lower than desired, if not compensated by a high thermostat strength γ . Since τ_H does not decay fast enough to zero for $\omega > \tau_F^{-1}$, one must choose a low cutoff frequency in order not to heat up the shells. As a consequence, the relaxation time for high-frequency phonons increases, making the effects of shell-induced drag more pronounced. However, the thermostat can be systematically improved by adding more degrees of freedom, so as to obtain a more sharply defined filter, as we will show below.

Thermostatting on *ab initio* CPMD is more challenging. Since wavefunctions are not atom-centered, the coupling of the dynamics of the electronic DOF to the ions is stronger than in the shell-model case, and the presence of high-frequency components in the noise quickly heats up the electrons. Furthermore, because of the expense of *ab initio* CPMD, it is mandatory to have fast equilibration and sampling. We will show that both problems can be solved thanks to the tunability and predictability of our scheme. As a test example, we ran simulations of a single heavy water molecule in vacuum, using a standard literature setup (see Fig. 3 and Ref. [21]). We ran several independent trajectories for a total of 90 ps, starting from ionic configurations equilibrated at 300 K and from wavefunctions quenched to the Born-Oppenheimer surface [22]. We have used Eq. (2) with 5 extended momenta and fitted **A** and **B** in order to obtain a short, optimal response time over the ionic degrees of freedom, and an abrupt increase in the region corresponding to electronic modes [see inset of Fig. 3(b)]. We then compare this case with results from a massive Nosé-Hoover-chains simulation [3, 23]. In both cases the strength of the thermostat is such that the underlying dynamics of the ions is severely altered.

With the present, very conservative choice of parameters the drift in electronic energy is negligible for both thermostats. In Figure 3 we plot the autocorrelation function of the squares of the normal modes. The integral of these functions measures the time required to lose memory of the initial configuration. It is evident that the use of an optimized colored-Langevin thermostat dramatically reduces this time.

The thermostat we have presented offers a number of advantages. It can be used in CP-like, extended-

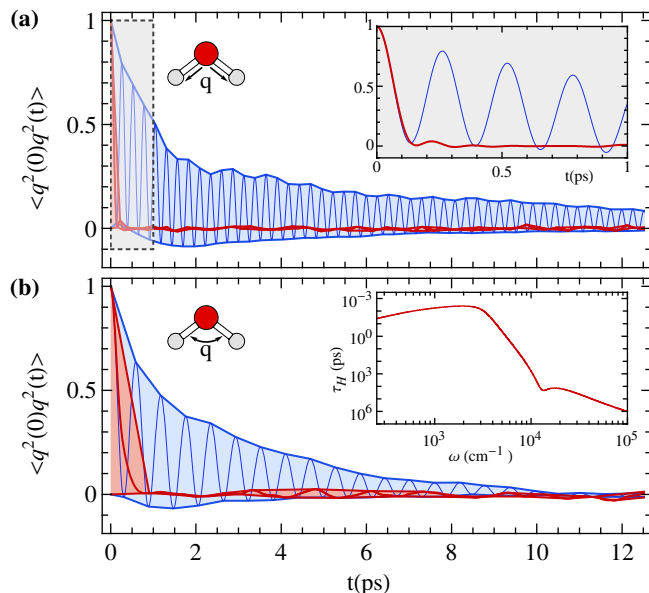


FIG. 3: (color online) Autocorrelation functions for the squares of (a) the symmetric stretching and (b) the bending modes of a heavy water molecule in vacuum, performed in the NVT ensemble at $T = 300$ K. We use a fictitious mass $\mu = 200$ a.u., and a timestep of 4 a.u., in order to minimize the errors on the forces [20]. The Nosé-Hoover thermostat with chain length 4 has been used, and its mass chosen so as to maximize the coupling to the stretching mode. The NH correlation functions (lighter lines, blue in the online version) are highly oscillating and decay very slowly. The shading highlights the curve's envelope. In contrast using the new thermostat (darker lines, red in the online version) we find a much sharper decay, which in the case of the stretching requires an enlarged scale to be appreciated [inset of panel (a)]. In the inset of panel (b) we show the relation between τ_H and ω for our thermostat. The parameters have been optimized to obtain a sharp decay of the response for frequencies above the stretching mode.

Lagrangian simulations, and it is also much faster in reaching equilibrium than the Nosé-Hoover thermostat. This is particularly relevant when performing expensive, *ab initio* simulations, but any problem which requires averaging over uncorrelated configurations of the system can greatly benefit from the enhanced relaxation time. The optimal parameters of the simulation can be easily estimated before the run is started. Here, in the difficult case of a molecule in vacuum, we have been able to reduce the correlation time down to a fraction of a picosecond. An additional advantage is that the exact propagator in the case of zero force is obtained easily [16], which makes the implementation simple and robust, at variance with Nosé-Hoover chains [3] which requires a high order integrator to ensure accurate trajectories [24]. Finally, the introduction of highly tunable, non-Markovian thermostats in molecular dynamics simulations lays the foundations for the development of optimal sampling algorithms, which can be of great benefit in free-energy techniques, or when one must treat systems with a broad vibrational spectrum, which is the case for instance in

path-integrals MD. We believe that this is only a first example, and that colored noise will find many other applications in a variety of computational problems. We thank Dr. G. Tribello for helping us in the simulation of calcium carbonate and for carefully reading the paper.

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